

RR I SLL
VL/VVL, CL

SLL 81 391

JASON

Technical Report
JSR-80-14

December 1980

VISIBLE CHEMICAL LASERS

By: N. Fortson
W. Happer
J. Katz

DISTRIBUTION STATEMENT A

Approved for public release;
Distribution Unlimited

DTIC QUALITY INSPECTED 4

19980309 356

SRI International
1611 North Kent Street
Arlington, Virginia 22209

PLEASE RETURN TO:
BMD TECHNICAL INFORMATION CENTER
BALLISTIC MISSILE DEFENSE ORGANIZATION
7100 DEFENSE PENTAGON
WASHINGTON D.C. 20301-7100

U38/6



Accession Number: 3816

Publication Date: Dec 01, 1980

Title: Visible Chemical Lasers

Personal Author: Fortson, N.; Happer, W.; Katz, J.

Corporate Author Or Publisher: SRI International, 1611 North Kent Street, Arlington, VA 22209 Report Number: JSR-80-14 Report Number Assigned by Contract Monitor: SLL 81 291

Comments on Document: Archive, RRI, DEW.

Descriptors, Keywords: Directed Energy Weapon DEW JASON Visible Chemical Laser Oxygen Iodine Nitrogen Halide Carbon Monoxide Nitrix Oxide Azide Magnesium Calcium Energy Level Photolysis Electric Power Supply

Pages: 34

Cataloged Date: Oct 19, 1992

Document Type: HC

Number of Copies In Library: 000001

Record ID: 25009

Source of Document: DEW

JASON

Technical Report
JSR-80-14

December 1980

VISIBLE CHEMICAL LASERS

By: N. Fortson
W. Happer
J. Katz



CONTENTS

1. Introduction.....	1
2. The Oxygen-Iodine Laser.....	4
3. Nitrogen Halides.....	7
4. Carbon Monoxide-Nitric Oxide.....	14
5. Azides.....	18
6. Magnesium-Calcium.....	24
References.....	31
Acknowledgements.....	31

LIST OF FIGURES

FIG. 1	Energy levels of Oxygen and Iodine. (Avizonis, AFWL).....	6
FIG. 2	Energy levels of the NF molecule and the Bismuth atom. Energy levels of the Iodine atom are shown for comparison. (Warren, Aerospace).....	9
FIG. 3	Photolytic (a) and chemical (b) sources of NF(a' Δ) molecules for chemical pumping of lasing atoms, e.g., Bismuth. (Warren, Aerospace).....	11
FIG. 4	Demonstration of $1^* + \text{NF}(a^1\Delta) \rightarrow 1 + \text{NF}(b^1\Sigma^+)$ Transfer at system concentration level. The NF(b $^1\Sigma$) molecules could serve as the upper state or as a chemical pump for a green chemical laser. (Warren, Aerospace).....	13
FIG. 5	Energy levels of the CO and NO molecules. (Rich, Calspan).....	16
FIG. 6	NO β and γ emission spectra for several He concen- trations in mixtures of He, CO and NO pumped by a CO laser. (Rich, Calspan).....	17
FIG. 7	Radiation from gas containing N ₃ . Vibrational sequences expected for N ₂ (1 $^+$), etc., are shown. (Taylor).....	21
FIG. 8	The red bands of the transition NCl(b $^1\Sigma$) \rightarrow NCl($\chi^3\Sigma$) produced by azide chemistry. (Kuhn, Rockwell).....	25
FIG. 9	Observation of Mg(3P) in Mg-N ₂ O flame. (Benard, AFWL).....	27
FIG. 10	Hypothetical Mg-Ca Energy Flow (Benard, AFWL).....	29

1. Introduction

For many years the potential utility of chemical lasers operating in the visible region of the spectrum has been obvious. The use of chemical fuels would eliminate the need for massive electrical power supplies, and visible light propagates with minimal diffraction spreading through the atmosphere. Much effort has been expended in trying to develop visible chemical lasers in the United States. After reaching an unsuccessful climax of activity in the mid-seventies, work on chemical lasers subsided to a low level. The recent development by the Air Force Weapons Laboratory of the oxygen-iodine laser operating at 1.31μ in the near infrared has stimulated renewed interest in the feasibility of visible chemical lasers.

In the spring of 1980 DARPA requested that JASON review the present status of research on visible chemical lasers. During the summer of 1980 a JASON committee spoke to a number of scientists with interests in areas related to visible chemical lasers. This report summarizes the most interesting ideas encountered during the summer. The committee found that excellent work is being carried out at several laboratories. The prospects for visible chemical lasers seem guardedly hopeful, although many key questions remain unanswered and no avenues of research seem so likely to succeed that a major increase in the research effort is warranted.

The lessons of the oxygen-iodine laser have not been lost on the community and much work has been devoted toward finding other systems which

have similar favorable characteristics. The useful electronic energy of the oxygen iodine lasers is generated because the ground state of the oxygen molecule is a spin triplet while most chemical reactions which produce oxygen molecules proceed along a singlet potential energy surface. Because the nuclear charge of the oxygen atom is relatively small, electronic spin is quite a good quantum number and the low-lying singlet states of the O_2 molecule are extremely metastable, even in solution. Thus, adequate time is available for the oxygen metastable molecules to transfer their energy to atomic iodine which has a sufficiently short radiative lifetime and a sufficiently narrow emission linewidth to lase on the fine structure transition $^2P_{1/2} \rightarrow ^2P_{3/2}$. The same spin-selection rule which makes $O_2(^1\Delta)$ molecules so metastable also makes it impossible for the O_2 molecule to lase on the transition $^1\Delta \rightarrow ^3\Sigma$ to the ground state. Even if the radiative transition were not so highly forbidden, the broad linewidth of the transition in molecular oxygen, which results from the large number of occupied vibration-rotation levels in the upper state, $^1\Delta$, of the metastable molecule and the large number of vibration-rotation levels to which lasing is allowed by the Franck-Condon principle, lead to a very broad stimulated emission linewidth and a correspondingly low gain.

The nitrogen halide molecules, in particular NF which is isoelectronic to O_2 , have received a great deal of attention. Nitrogen halides have $^1\Delta$ and $^1\Sigma$ metastable states like O_2 ; they can be generated by chemical reactions similar to those which produce metastable O_2 ; and atoms, e.g., bismuth, can be found which have energy levels

resonant with metastable NF . One should not be blinded to other possibilities by the success of the oxygen-iodine laser. Good work on chemically excited metal oxides and metal atoms is being pursued at the Air Force Weapons Laboratory. Interesting work on vibrational to electronic energy transfer is proceeding at Calspan. Excellent computational resources are available, for example, at the National Bureau of Standards where the group headed by M. Krauss has had much successful experience in calculating key molecular parameters.

After evaluating the information received during the summer, the JASON committee reached the following conclusions:

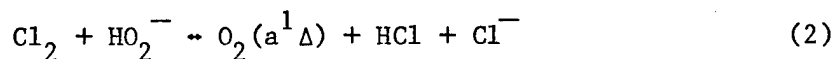
- A. Visible chemical lasers cannot be ruled out on the basis of any known scientific laws, and indeed the success of the oxygen-iodine laser gives encouragement that other chemical lasers at still shorter wavelength may be found.
- B. There is no obvious area which, if heavily funded, would very likely lead to new visible chemical lasers. Thus, no large new program on visible chemical lasers can be justified at this time.
- C. There are a few good ideas for new visible chemical lasers; for example, the work on NF at Aerospace, the work on metal oxides at the Air Force Weapons Laboratory, and the work on CO-NO at Calspan. Modest support of work in areas like these would be a good investment, since it would encourage continued awareness of DOD needs for visible chemical lasers.
- D. It would not be in the best interests of the DOD to have work on new visible chemical lasers stop completely. The history of

the oxygen-iodine laser at the Air Force Weapons Laboratory shows the wisdom of long-term funding of good but slowly maturing new ideas.

2. The Oxygen-Iodine Laser

The O_2 -I electronic transition chemical laser was developed at the Air Force Weapons Laboratory and is the only such laser in existence. At a wavelength of 1.31μ it is not quite "visible," but presents many of the same problems faced by any electronic transition chemical laser. That it works at all is seemingly miraculous, for it depends on a number of fortunate reaction rates.

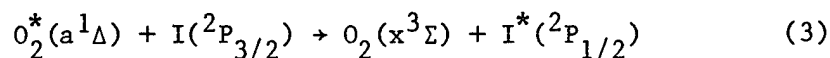
Energy is stored by the first excited state of $O_2(a^1\Delta)$. This highly metastable state has a radiative lifetime of about 45 minutes, essentially infinite. It is also nearly immune to deactivation on many surfaces and in most collisions and may flow through pipes almost as if it were a stable gas. It may be produced in an alkaline solution of H_2O_2 by the addition of Cl_2 in the following reactions:



The second reaction has a quantum yield near 100%, presumably because all species have zero spin. Spin conservation then prevents the formation of ground state $O_2(x^3\Sigma)$ in reaction (2).

Aqueous solutions are messy things, in which spin conservation may not be exact, so $O_2(a^1\Delta)$ may be de-excited. The de-excitation rate has been measured, and is quite slow, with a time constant of about 2 μ sec. If Cl_2 gas is bubbled through the alkali-peroxide solution then reaction (2) will take place in solution near the surface of the bubbles. $O_2(a^1\Delta)$ may diffuse back into the bubbles and be convected out of the liquid. Quantum yields for the production of $O_2(a^1\Delta)$ of 40% have been reported, and a metastable density of 0.3 torr (10^{16} cm^{-3}) has been measured in the gas phase above the solution.

Figure 1 shows the relevant energy levels. $O_2(a^1\Delta)$ is resonant with the first excited state ($^2P_{1/2}$) in the I atom, so the reaction



occurs rapidly. The spontaneous radiative decay of excited I is slow (the lifetime is about 0.1 second for this magnetic dipole transition), so it is possible to pump an inversion in I atoms with a reasonable density of metastable O_2 , even though the lower lasing level in I is the ground state.

Iodine is ordinarily diatomic, and some energy is required to break up diatomic iodine molecules into iodine atoms. Fortunately (and fortuitously) the following reactions dissociate molecular I_2 :

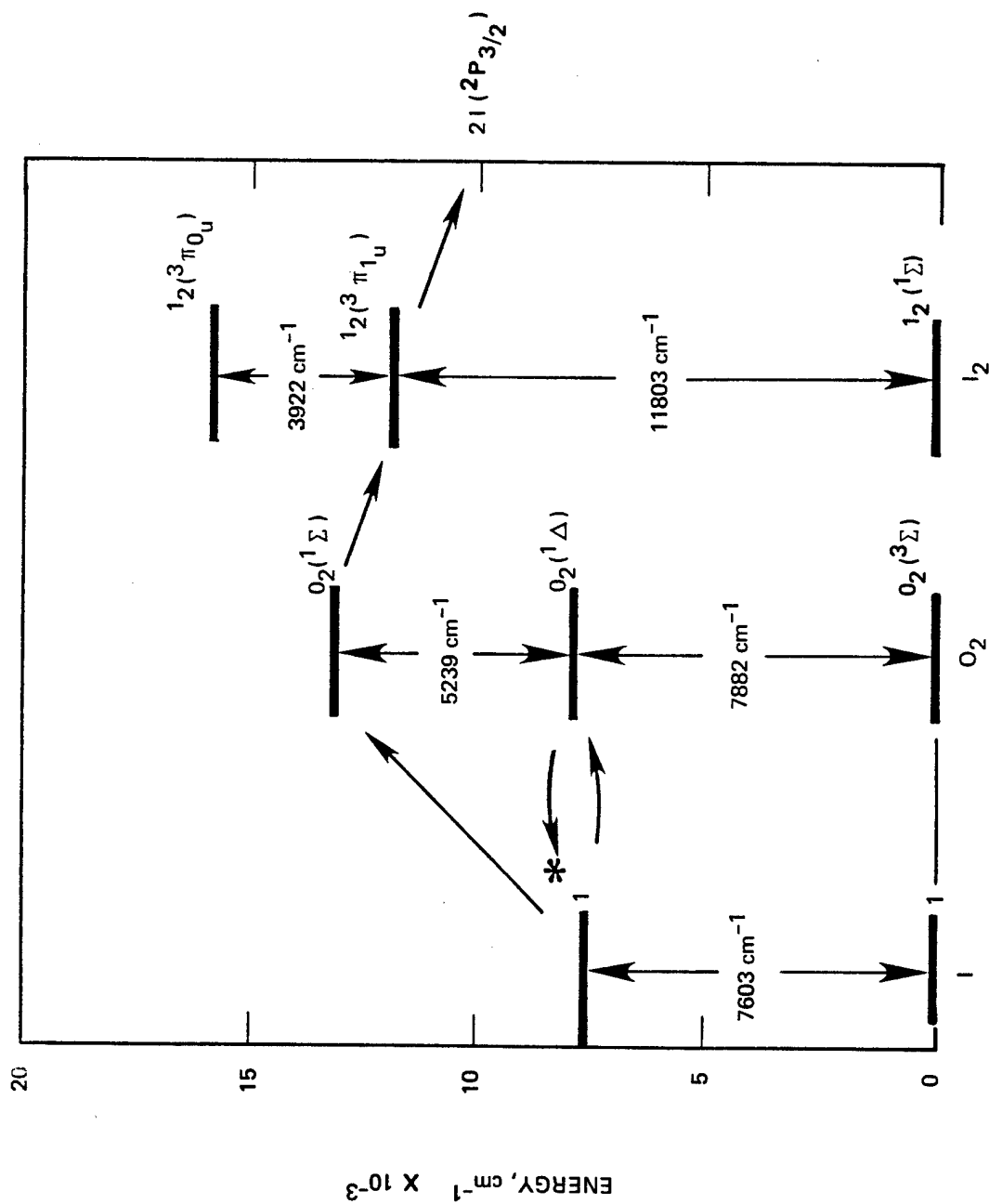
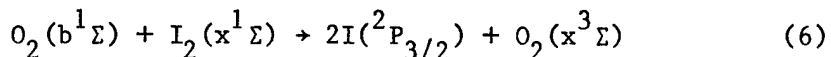
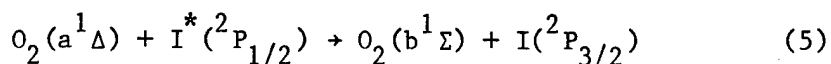
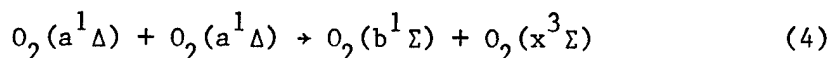


Figure 1 Energy levels of Oxygen and Iodine (Avizonis, AFWL)

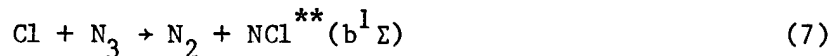


Reaction (4) is spin-forbidden and slow, while (5) depends on the low density of I^* . The highly excited $\text{O}_2(b^1\Sigma)$ generated through either pathway can dissociate I_2 .

The rates of these reactions, and others necessary for the understanding of gas phase kinetics of O_2 , I_2 , and I are well measured. The aqueous chemistry is less well understood, but well enough to use it as a "black box" source of $\text{O}_2(a^1\Delta)$.

3. Nitrogen Halides

Nitrogen halides, like NF , are isoelectronic to O_2 and they have the same metastable $^1\Delta$ and $^1\Sigma$ states as O_2 . It is possible to produce excited states of nitrogen halides in a variety of different reactions. In Section 5 on azides we discuss reactions like



and



It is also possible to produce excited NF in the reaction



Reaction (9) is of particular interest because it is known to produce NF^* with high efficiency. It may also be adaptable to the large scale combustor technology used in the HF laser.

NF_2 is readily produced by the thermal decomposition of N_2F_4 , a chemical which may be purchased commercially.

Figure 2 shows the lower potential curves of NF. The $a^1\Delta$ state has a spontaneous radiative lifetime of over a second. If it did emit a photon its wavelength would be 8740 Å, but because of the extremely small oscillator strength of this transition, its stimulated emission cross-section is insignificant and it cannot lase. The same is true for $\text{O}_2(a^1\Delta)$ (NF and O_2 are isoelectronic, and the electronic states correspond closely), but this metastable state is still useful, for it can be used to pump the I atomic laser. $\text{NF}(a^1\Delta)$ carries more energy than the corresponding state in O_2 so one might hope to couple its energy to an atomic species which can lase at a shorter wavelength. Fortunately, it is resonant with the first excited state of $\text{Bi}(^2\text{D}_{3/2}^o)$. If the pumping rate is high enough, it might be possible to invert Bi atoms and to produce a laser at 8760 Å, in close analogy to the atomic I laser at 1.31 μ.

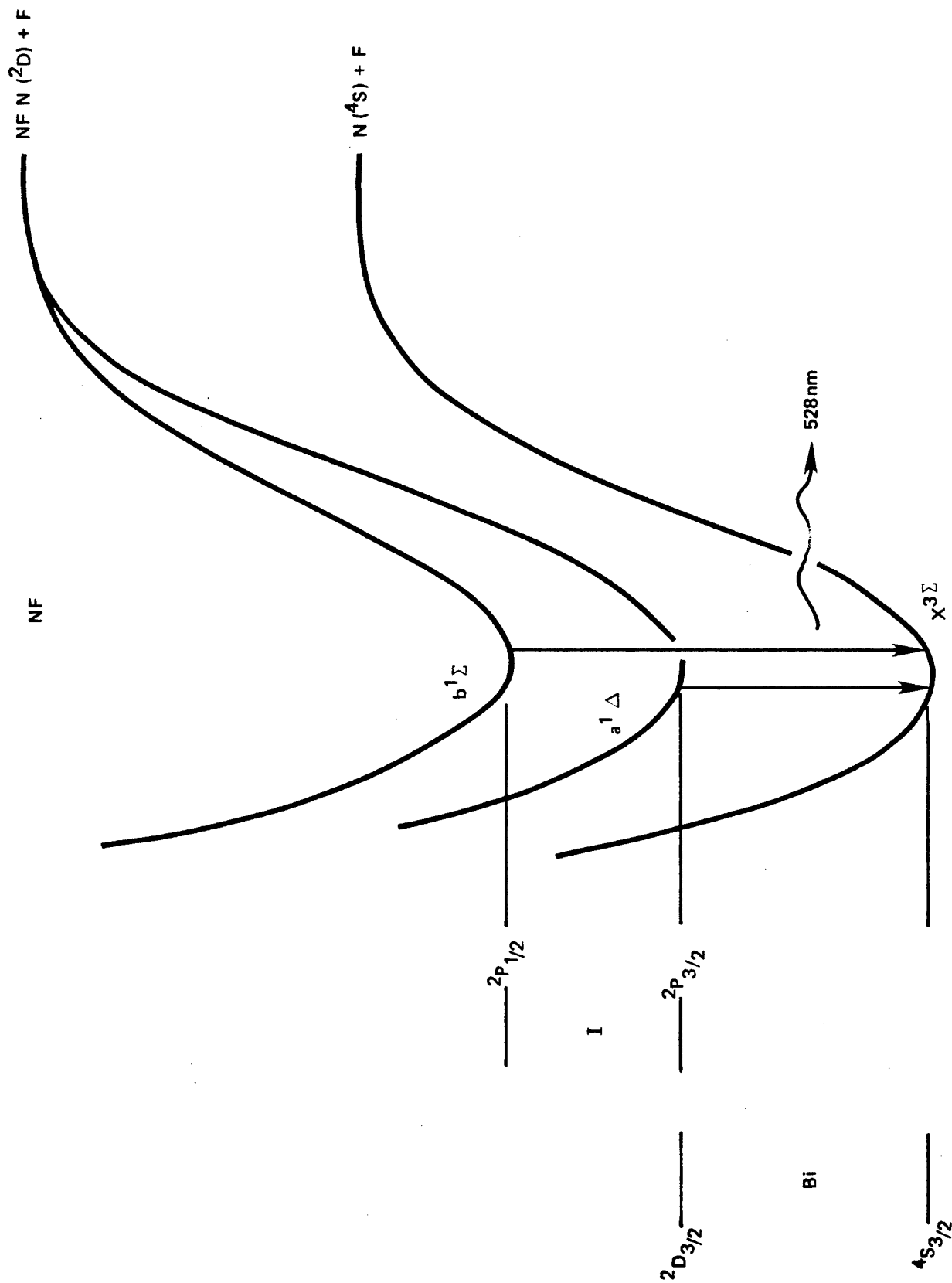
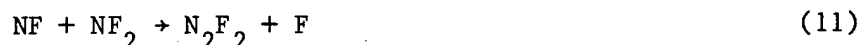


Figure 2 Energy levels of the NF molecule and the bismuth atom. Energy levels of the iodine atom are shown for comparison. (Warren, Aerospace)

In one respect the O_2^* and NF^* generators are quite different; O_2^* is produced in aqueous solution, while the more reactive fluorine compounds which produce NF^* must be handled in the gas phase. Reaction (9) requires H atoms which are hard to obtain. Fortunately, it may be possible to regenerate them, using them only as a catalyst, with the following reactions



In this way reactions (9), (10), and (11) react H_2 and NF_2 to produce N_2F_2 , HF and energy in the form of excited Bi atoms. Such a laser system would not be purely chemical because a certain number of H or F atoms are needed to initiate the cycle, and replenish losses. These atoms may be supplied by flash-lamp or excimer laser photolysis of NF_2 or by a discharge in NF_3 . If the losses of monatomic species are small, then the amount of electrical or photon energy required is small, and the laser system is almost entirely chemical. Alternatively, F atoms may be supplied chemically from the reaction between H_2 and NF_3 in a continuously reacting system.

Fig. 3 shows two conceptual designs of NF-Bi laser systems presented by the group at Aerospace, led by W. Warren. They hope that it will be possible to apply the nozzle and flow hydrodynamic technology developed for HF lasers. Fig. 3a shows a concept for a pulsed laser in

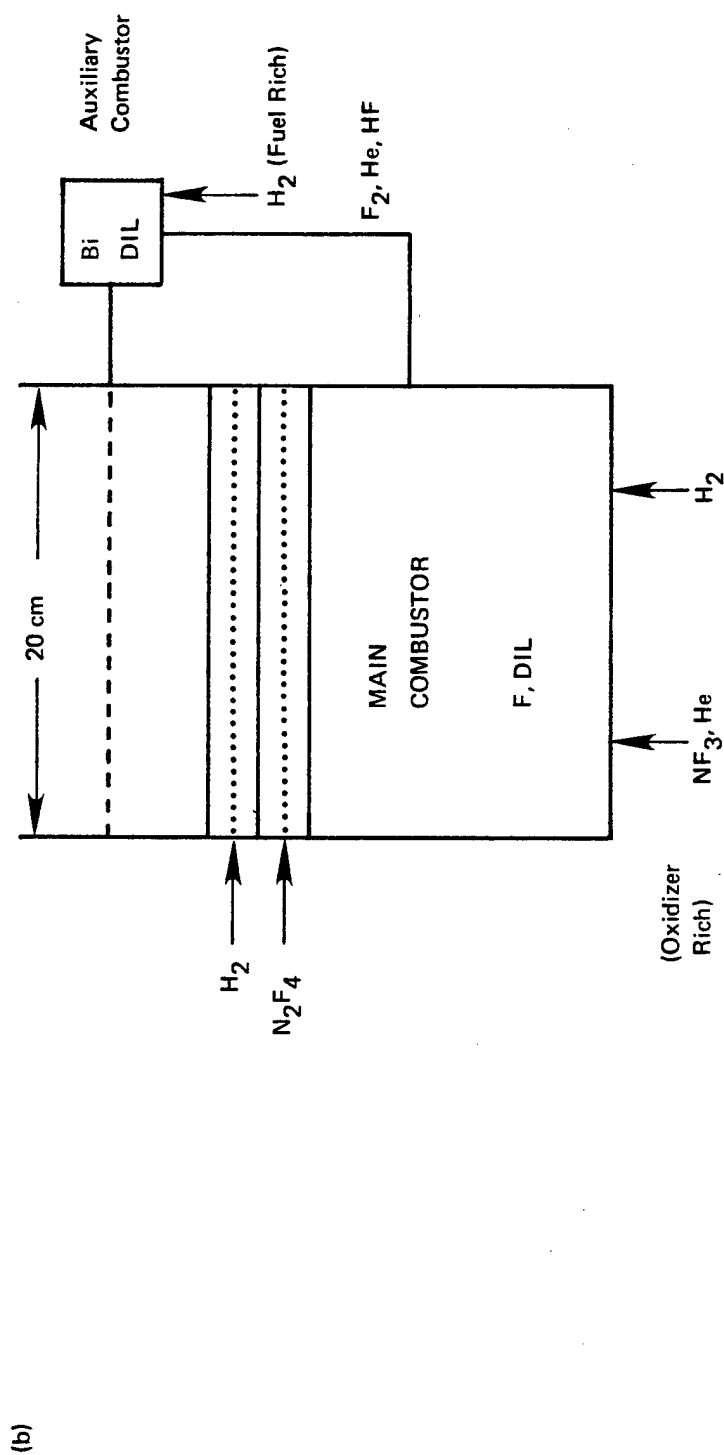
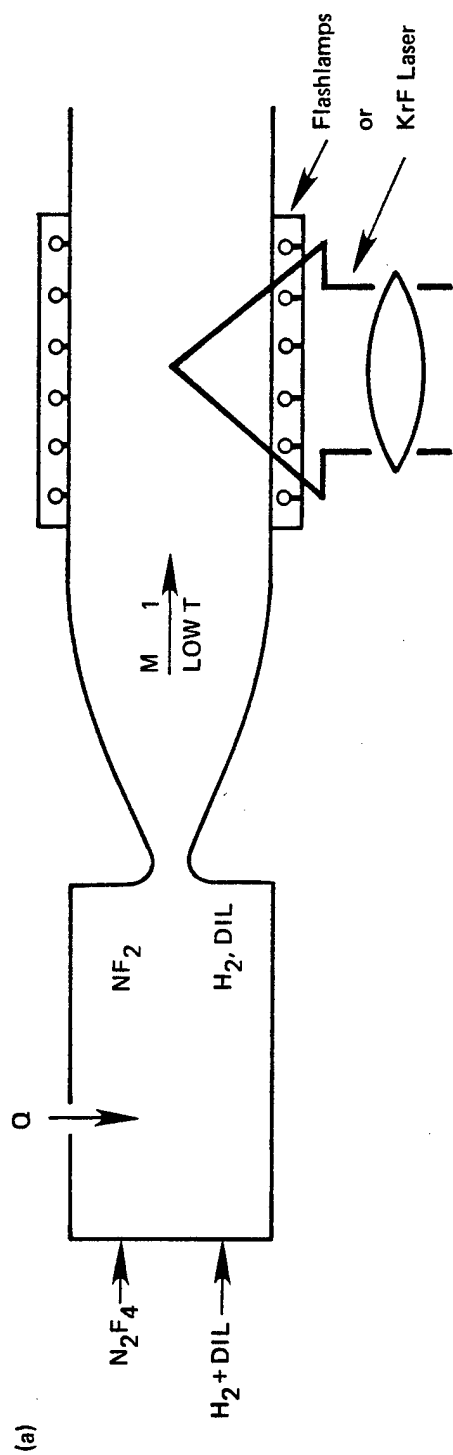


Figure 3 Photolytic (a) and chemical (b) sources of $\text{NF}(a^1\Delta)$ molecules for chemical pumping of lasing atoms, e.g., Bismuth. (Warren, Aerospace)

which external sources of heat and light are required (to dissociate N_2F_4 and photolyse NF_2), while Fig. 3b is an entirely chemical system, more suitable to a CW laser in which chemical reactions provide both the necessary heat and the F atoms.

The near infrared NF-Bi laser would be a substantial improvement in wavelength over $\text{O}_2\text{-I}$, but still shorter wavelengths are desirable. The energy difference between the $\text{NF}(a^1\Delta)$ and $b^1\Sigma$ states is almost exactly resonant with the excitation of $\text{O}_2(a^1\Delta)$ or the I atom. Thus, it may be possible to use energy pooling reactions between excited states of O_2 , I, and NF to produce $\text{NF}(b^1\Sigma)$, and to use the energetic $\text{NF}(b^1\Sigma)$ molecules to make a green laser. The Aerospace group has demonstrated that it is possible to use the light of an I laser to excite the $\text{NF}(b)$ state from the a state. Fig. 4 shows the evidence. The resulting apparatus is complex but not necessarily impractical. It would be desirable to transfer the excitation chemically, but we do not know how to do this; the direct reaction between excited NF and O_2 is spin forbidden (though that between NF and I is allowed), and various destructive side reactions are also possible in such a complex mixture. $\text{NF}(b^1\Sigma)$ might be used to make a laser directly, for it is less metastable than the a state and has a larger stimulated emission cross-section, or it too might be used as a storage medium to couple energy into some other suitable species.

The NF-Bi laser concept builds on the established chemistry of the $\text{O}_2\text{-I}$ laser system and on the gas-dynamic technology established in

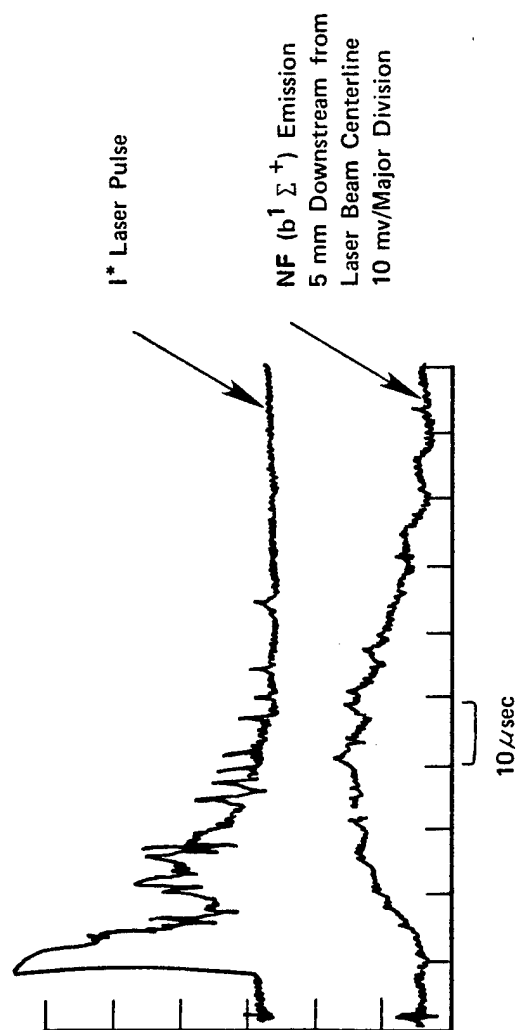


Figure 4 Demonstration of $1^* + \text{NF}(a^1\Delta) \rightarrow 1 + \text{NF}(b^1\Sigma^+)$. Transfer at System Concentration level. The $\text{NF}(b^1\Sigma)$ molecules could serve as the upper state or as a chemical pump for a green chemical laser. (Warren, Aerospace).

HF lasers. The basic reactions are reasonably well understood, at least qualitatively. This was one of the few areas considered worthy of further work by the Huestis memorandum¹ in 1976. The use of $\text{NF}(a^1\Delta)$ to pump Bi atoms is a possible solution to the problem of the insignificant gain of $\text{NF}(a^1\Delta)$ itself. Unfortunately, quantitative kinetic information is scarce, and may be the limiting factor in further development. The utility of the $\text{NF}(b^1\Sigma)$ state is more speculative but certainly is a worthwhile subject for basic research.

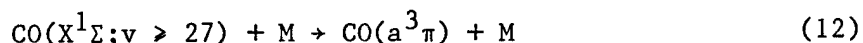
4. Carbon Monoxide-Nitric Oxide

Interesting work on mixtures of CO and NO is being carried on at Calspan by W. Rich and co-workers. The CO-NO system is not really a chemical laser, because it is pumped by a CO laser. However, it is worth briefly considering because it involves a process, vibrational to electronic energy conversion, which may be of importance in some chemical laser systems. Many exothermic chemical reactions produce vibrational, instead of electronic, excitation, so it is important to see if vibrational energy can be used to make an electronic transition chemical laser. For example, the very exothermic reaction $2\text{N}_3 \rightarrow 3\text{N}_2$ may feed all of its released energy into vibration.

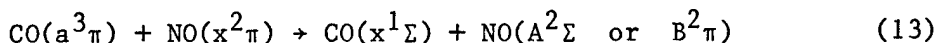
If the vibrational laser levels of CO vibration are pumped by the radiation of a CO laser, a series of nearly resonant energy exchange processes pumps a significant number of CO molecules into very high vibrational states. Coupling of vibrational to transitional motion is very weak, and the energy exchange processes are slightly exothermic, so that

the reverse processes cannot proceed if the transitional temperature is low. Fig. 5 shows the level diagrams of CO and NO. Infrared emission spectra have established that CO molecules are pumped up to vibrational levels with $v \gtrsim 30$; a small amount of He gas, as shown by the horizontal dashed lines, provides some vibration-translation relaxation and reduces the degree of excitation.

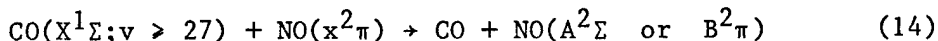
If NO is added to this highly vibrationally excited gas of CO, its β and γ emission bands are seen, and are shown in Fig. 6. The mechanism is not clear. One possibility is



followed by



but (12) is slow unless M has non-zero spin. Another possibility is



NO(A) cannot make a laser, but NO(B) might, if vibrational relaxation of NO($x^2\pi$) is fast enough. Preliminary estimates (by Rich, of Calspan, who also did this experimental work) suggests that gains will be uncomfortably small. The subject is still worth pursuing as a basic research problem, for the kinetics are interesting and (aside from CO vibrational pumping) not understood.

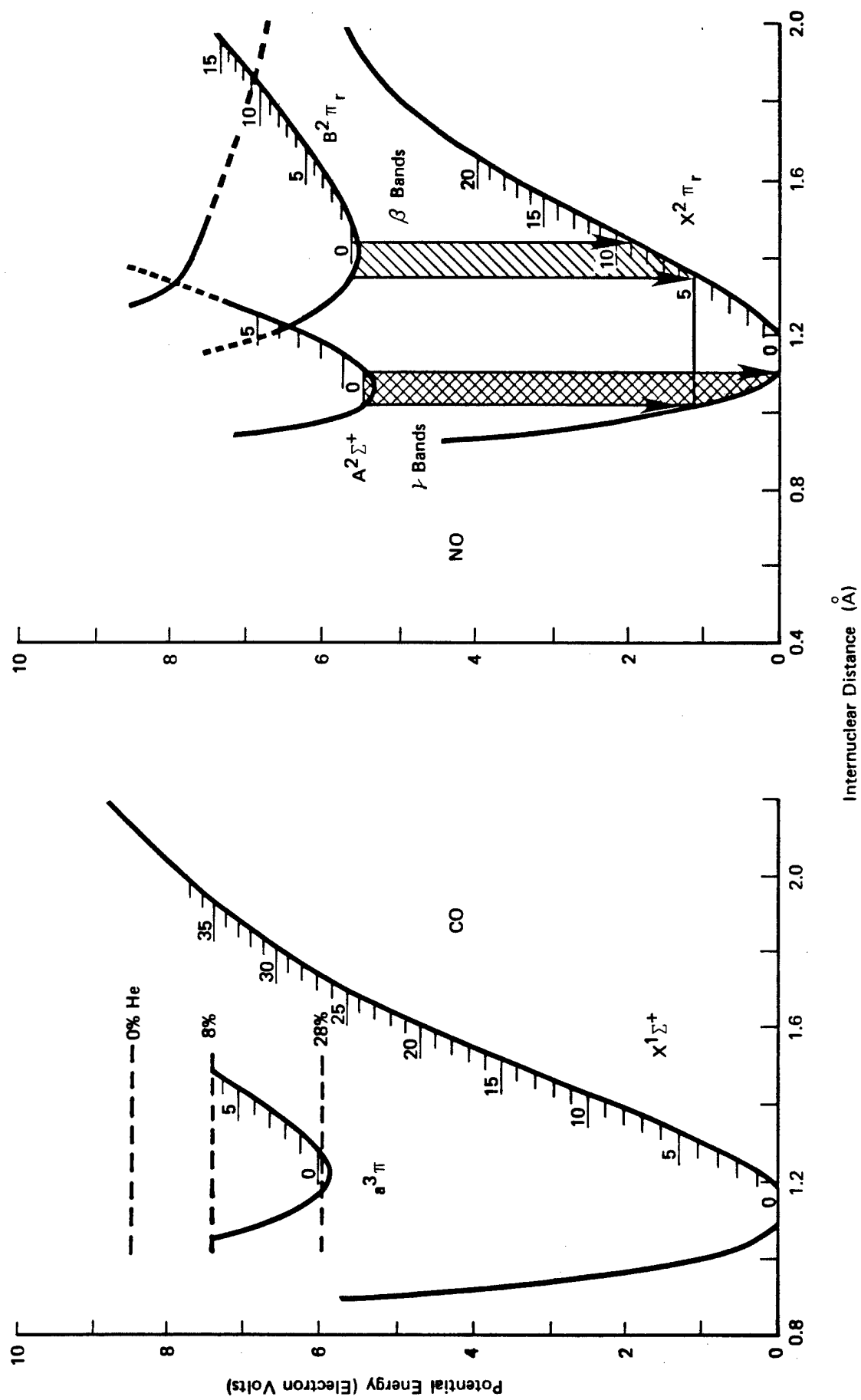


Figure 5 Energy levels of the CO and NO molecules (Rich, Calspan)

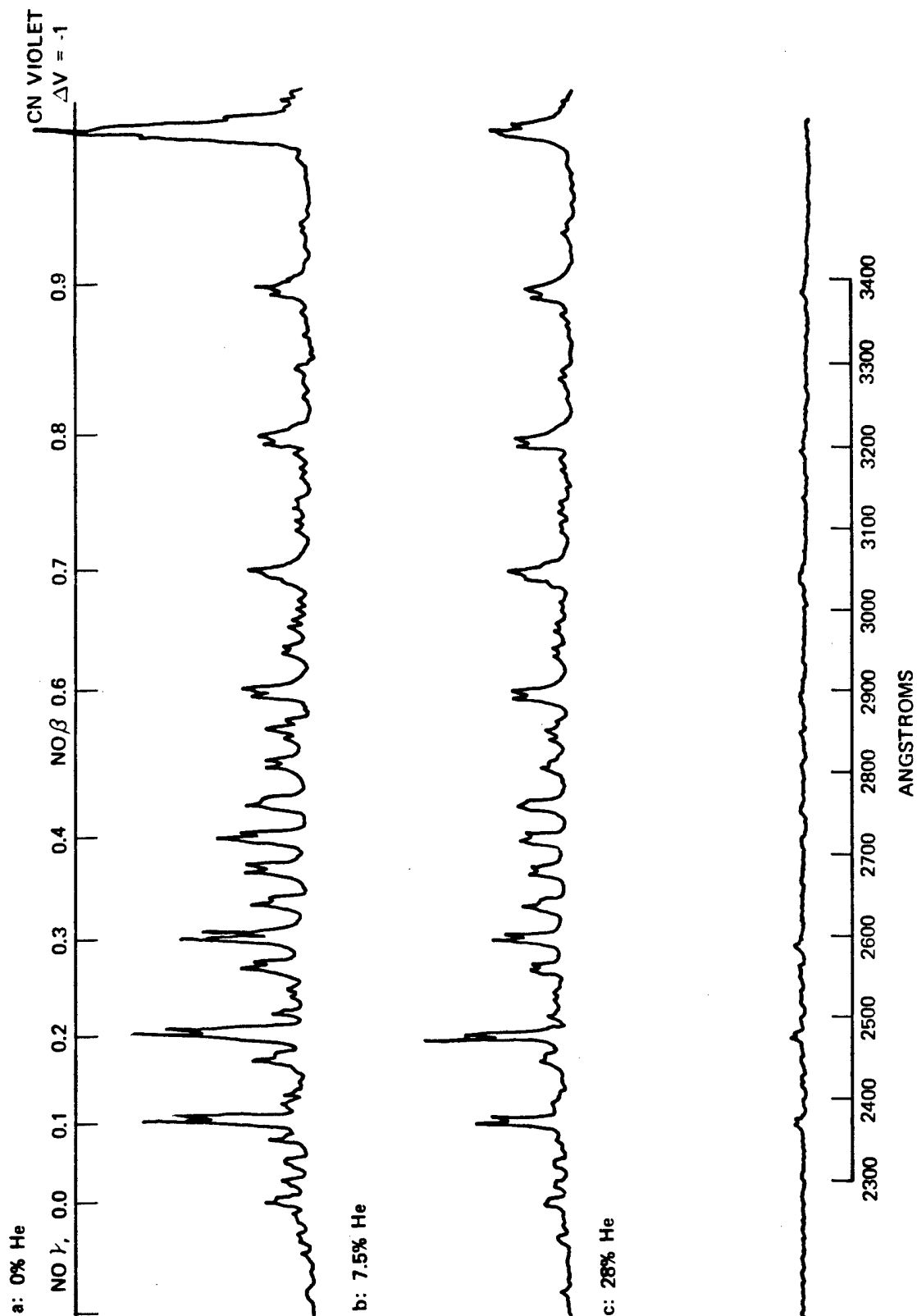


Figure 6 No β and γ emission spectra for several He concentrations in mixtures of He, CO and NO pumped by a CO laser. (Rich, Calspan)

5. Azides

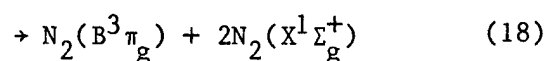
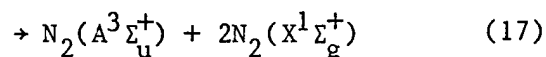
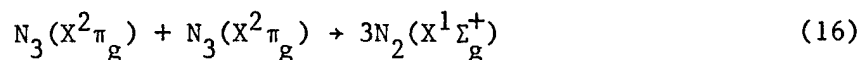
The azide radical, N_3 , and its compounds are natural candidates for making a visible chemical laser. Nitrogen atoms are most stable when bound into ordinary N_2 molecules with strong triple bonds; its dissociation energy of 9.8 eV makes N_2 among the most strongly bound molecules in existence. The reaction



releases 8.8 eV if all species are in their ground states. There is enough energy available from reordering the nitrogen atoms in azide radicals to make a visible, or even an ultraviolet laser. Despite all this stored potential energy, many azide compounds are quite stable, readily obtained, and safely handled. These include ionic azides like NaN_3 . Covalent azides may be generated in the laboratory. Some azides, like $Pb(N_3)_2$, are explosive, of course.

Having a strongly exothermic chemical reaction is far from sufficient for making a laser. It is necessary to create electronically excited atoms or molecules from this energy, and to produce an inversion with sufficient net gain. Ray Taylor reported on some experiments he performed at Physical Sciences, Inc. By heating NaN_3 a steady flow of N_3 radicals is obtained (verified by observing NO chemiluminescence if O atoms are introduced); the Na vapor which is also produced condenses on the walls of the apparatus. Flowing inert carrier gas carries the N_3 through the experimental apparatus.

If a sufficiently high density of N_3 is obtained the following chemical reactions may take place:



There is no a priori way to determine the branching ratio of these reactions. Contrary to the published statement of Piper, Krech, and Taylor, all these reactions are spin-allowed. The A and B states are excited above the ground state by 6.3 and 7.4 eV respectively (for zero vibrational quantum number). The B state rapidly radiatively decays to the A state. The A state is metastable because LS coupling is an excellent approximation for such low Z atoms, and it is of different multiplicity from the only state (X) to which it can decay. If it is produced in sufficient quantity $N_2(A^3\Sigma_u^+)$ may be very useful, because it stores energy which might be transferred to some lasing species. (It is highly unlikely that $N_2(A)$ itself could lase because its transition is so forbidden and is broadened by vibrational and rotational structure and because of the unavoidable presence of large quantities of ground state N_2).

Having created a sufficient density of N_3 , one must try to determine the relative branching ratios into reactions (16), (17), and

(18), or at least the rate of the useful reactions (17) and (18). One might measure the density in state A using its absorption spectrum. This has not been done, and the only evidence available to us comes from Taylor's search for the emission of radiation in the B to A transition, known as the first positive band $N_2(1^+)$. If detected, this would imply that reaction (18) is taking place. The evidence is shown in Fig. 7. Taylor suggests that the broad emission in the red is $N_2(1^+)$, and indicates the expected position of various vibrational sequences above the curve. We are quite skeptical, for the shape of the curve is not that of familiar band spectra, nor does it even correspond to the expected sequences. We have not seen a confirmed spectrum of $N_2(1^+)$ with this appearance. The unidentified band in the blue (and another, not shown, in the ultraviolet) seem to imply contamination, and force us to conclude that the case for any production of electronically excited N_2 is unproven. There is no doubt that excited $NO(A^2\Sigma^+)$ may be produced, but this is of no interest for making a laser because of its rapid allowed decay to the ground state. If $NO(B^2\Sigma\pi)$ is produced it may be of more interest, because it decays to excited vibrational levels of the ground state.

It may be possible to use the energy stored in the azide radical to create metastable electronically excited species other than N_2 . Although these don't have as much energy as excited N_2 , they usually have about 2eV, enough to suggest that a red or near-IR laser might be possible. Possibly the simplest and most direct scheme is to photolyse a covalent azide such as ClN_3 . This couldn't lead to a completely chemical laser, because of the need for photons but is worth considering, even if

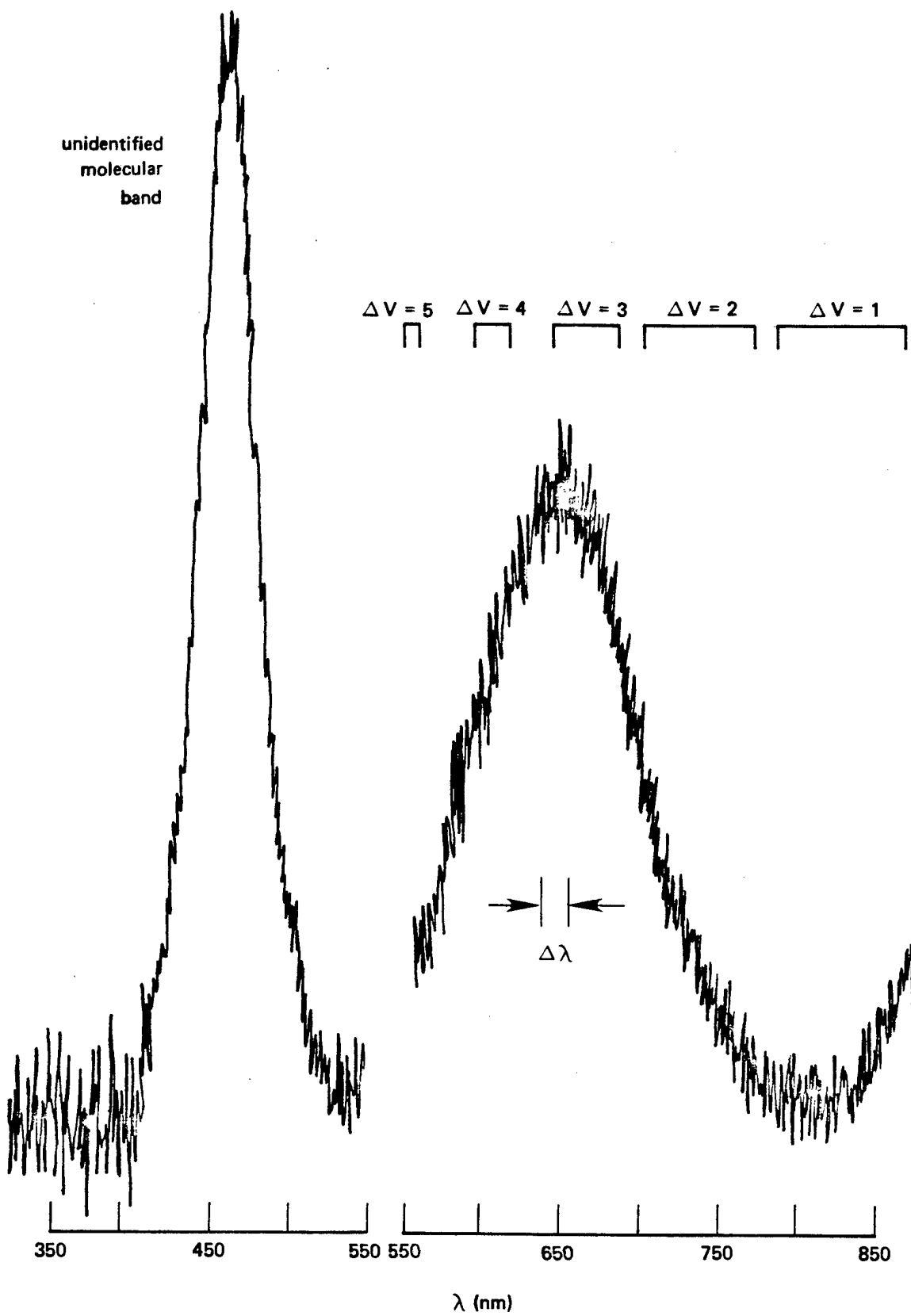
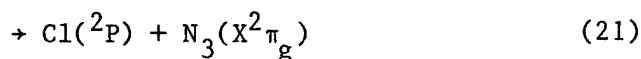
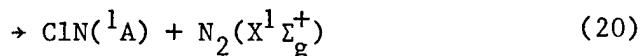
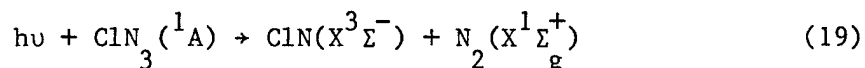


Figure 7 Radiation from gas containing N_3 . Vibrational sequences expected for $N_2(1^+)$ etc. are shown. (Taylor)

only as an experiment in kinetics. The easiest bond to break is the one between N_2 and the rest of the molecule; this generally requires less than 1 eV, while detaching the N_3 from the Cl requires 1.6 eV, and substantially more if other atoms or radicals are substituted for the Cl. One may consider three types of reactions:

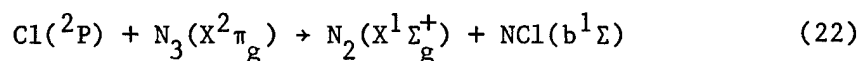


Reaction (19) requires the least energy, but has a negligible cross-section because it is spin-forbidden. Reaction (20) is allowed and requires less than 2eV; $ClN(^1A)$ refers to all low-lying singlet states. The last reaction is useless and a parasitic loss of photons but has a higher threshold than (20). Therefore, efficient production of metastable singlet ClN is promising via reaction (20). One might consider using either a single UV photon (the ClN_3 absorption is insignificant for wavelengths longer than 3000 Å) or many infrared laser photons to accomplish this.

Taylor attempted to produce the $b^1\Sigma^+$ state of ClN via flash-lamp induced reaction (20). This state has lifetime of a few ms to radiative decay to the ground state. This is shorter than the lifetimes of metastable states in lighter molecules (NF and O_2 , for example), because of the higher Z of Cl but still long enough to permit coupling

the energy to some lasing species; spontaneous fluorescence should be detectable. The lowest vibrational state stores 1.86 eV, so $\text{ClN}(\text{b}^1\Sigma^+)$ fluoresces in the red (0-0 is near 6650 \AA). Taylor was not able to find convincing evidence of this fluorescence.

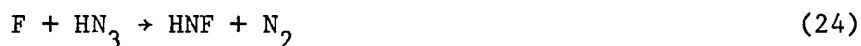
More promising may be attempts to produce metastable NCl and related compounds chemically. There are a number of ways of doing this, but here we consider only processes based on azides. One may consider two series of reactions. The first proceeds through the azide radical.



N_3 may be made thermally by decomposition of NaN_3 , or chemically:



A possible alternative is



Reactions (24) and (25) can only produce excited NF because of spin conservation.

Bob Kuhn at Rockwell Science Center has observed the red bands of $\text{NCl}(b^1\Sigma) \rightarrow (X^3\Sigma)$ from reactions (22) and (26) (see Fig. 8).

Metastable $\text{O}_2(a^1\Delta)$ has been successful in pumping the I atomic laser. For that reason analogous species like NF and $\text{NCl}(a^1\Delta)$ are of interest as are other metastables like $(b^1\Sigma)$. It is possible to consider lasing either in the nitrogen halide molecule or in an atom (such as Bi) to which excitation is transferred. NF(a) is too metastable to lase itself, but other states or species are not ruled out. Azide reactions are one way of producing them, but must compete with alternative chemical processes.

In summary, azides are worth investigating as candidate fuels for visible chemical lasers. At present their reaction kinetics are almost entirely unknown and must be considered a problem in basic research. The first step which should be taken is to measure the rates of their reactions. It is important that the effort to make these measurements have sufficient support and duration to carry the work to its conclusion. An effort like Taylor's, which is terminated when a few tantalizing hints have been observed, is wasted.

6. Magnesium-Calcium

Dr. D. Benard at AFWL has reported building a chemical flame generator for metastable Mg atoms in the lowest excited 3P state. He would like to use these metastable atoms, each containing 2.7 eV, to excite Ca atoms. The excited $\text{Mg}(^3P)$ is energetically resonant with $\text{Ca}(^1D)$.

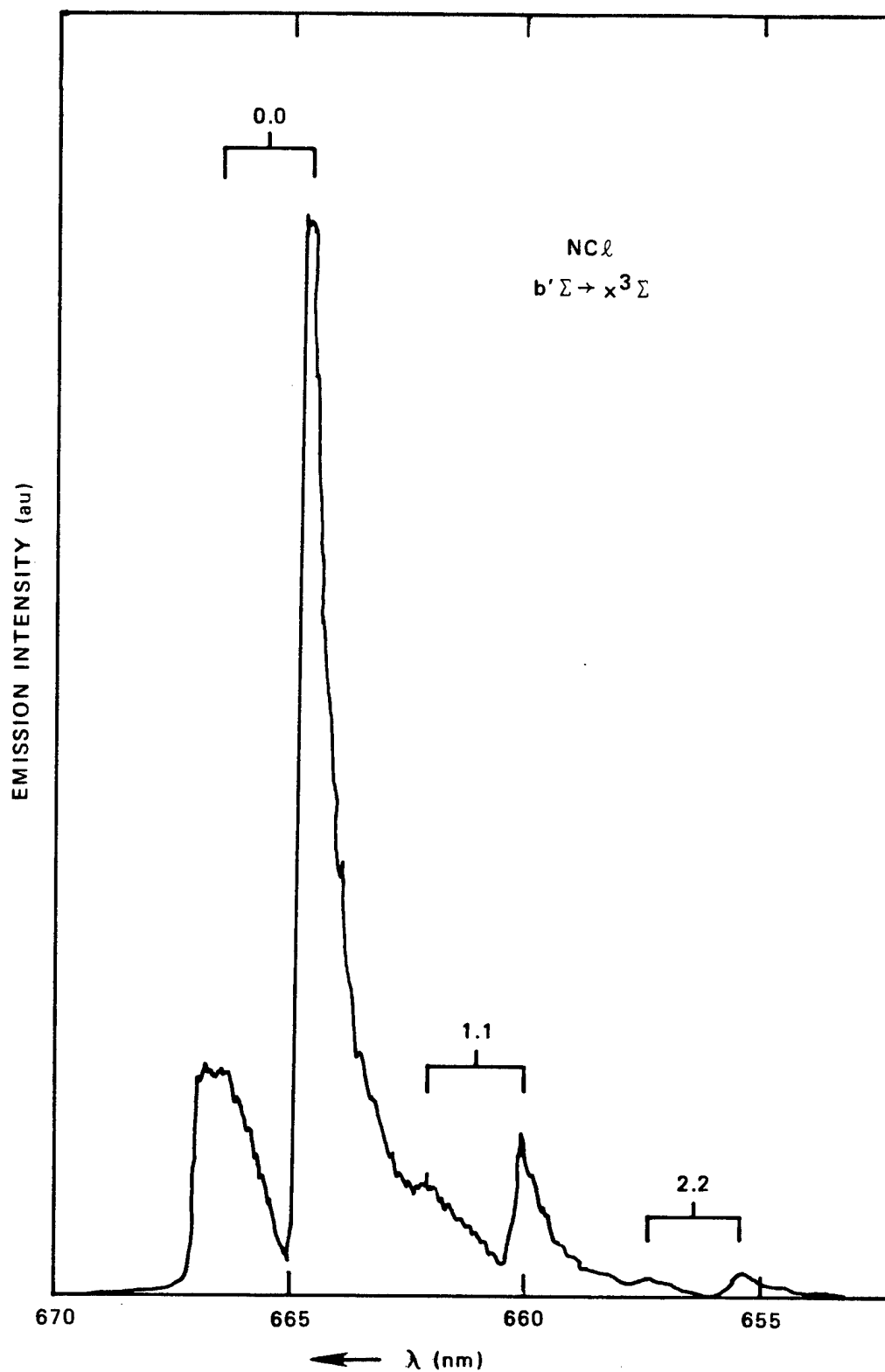
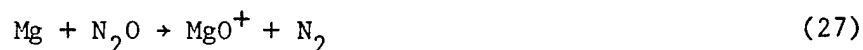


Figure 8 The red bands of the transition $\text{NC1}(b'\Sigma) \rightarrow \text{NC1}(x^3\Sigma)$ produced by azide chemistry. (Kuhn, Rockwell)

After the latter is collisionally de-excited to the 3D state, which radiatively decays to the 3P state, he hopes to invert the 3P states of Ca with respect to the 1S ground state. Although forbidden, this last transition has enough oscillator strength ($A = 2600 \text{ s}^{-1}$) to make significant gain possible if an inversion can be obtained. This is in contrast to molecular forbidden transitions which have their limited stimulated emission cross-section spread over a broad vibrational and rotational structure.

Benard reports the formation of $\text{Mg}(^3P)$ in a $\text{Mg-N}_2\text{O-CO}$ flame. His evidence, shown in Fig. 9, is persuasive. Unfortunately, the mechanism is obscure. He suggests reactions:



The $^+$ denotes a vibrationally excited species. In reaction (28) all species, except Mg^* , are singlets; Mg^* is a triplet. This ought to make the rate of (28) small, while the production of ground state Mg should be rapid. An analogous series of reactions producing Na^* is known to proceed, but that is expected because both NaO and Na^* are doublets.

By introducing Ca vapor into the gas flow containing Mg, transfer of excitation is hoped for.

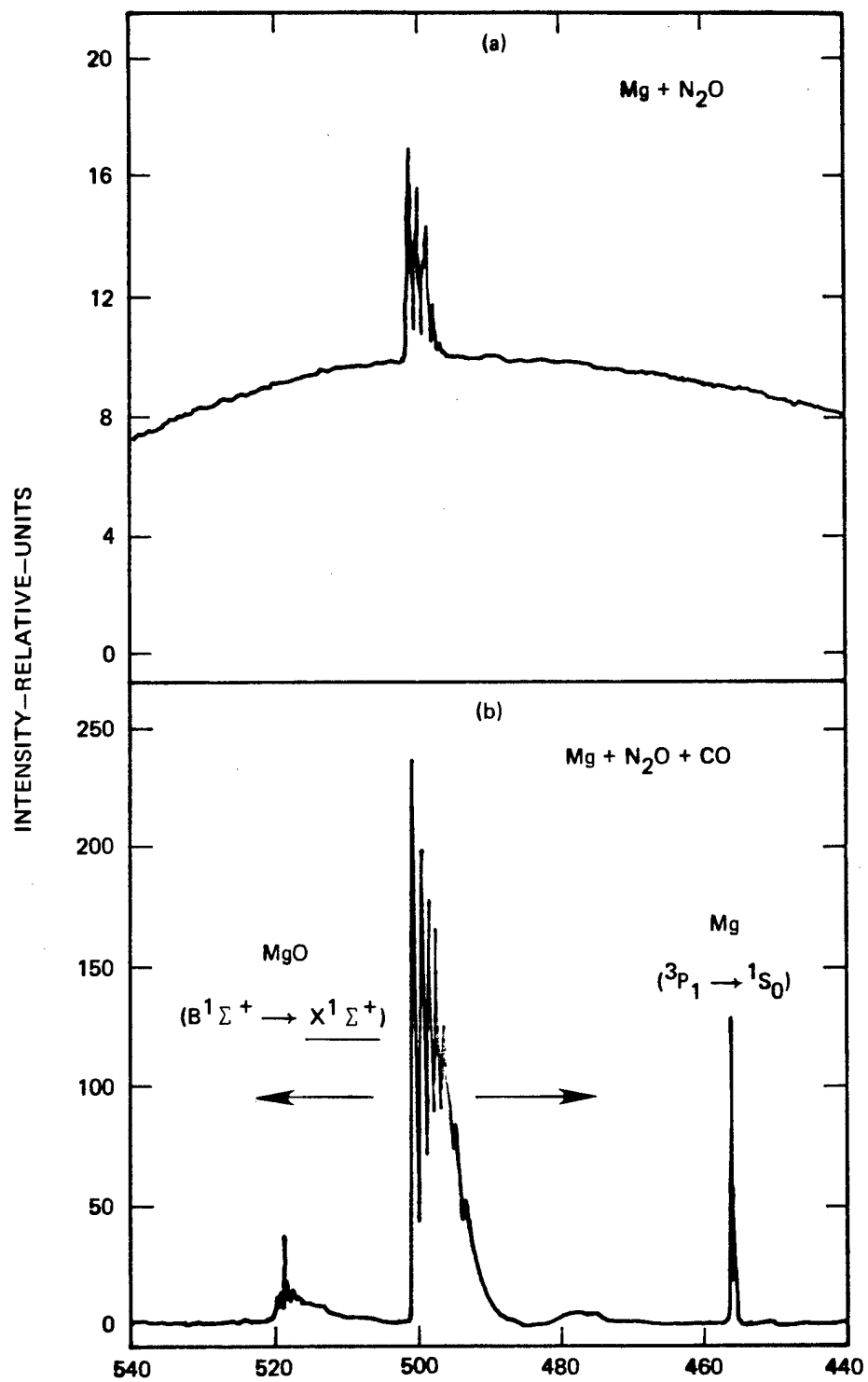
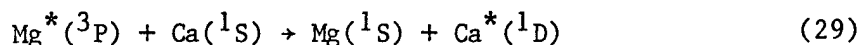


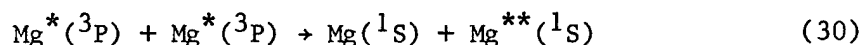
Figure 9 Observation of Mg(³p) in Mg-N₂O flame. (Benard, AFWL)



Even though this reaction is energetically resonant (the right hand side has 21850 cm^{-1} , and the left hand side between 21850 cm^{-1} and 21911 cm^{-1} , depending on J) it is spin forbidden. As a result we find the reported rate constant of $3 \times 10^{-11} \text{ cm}^3/\text{sec}$ surprisingly large.

Benard then depends on collisional relaxation from ^1D to ^3D ; at a wavelength near 7μ the forbidden radiative decay is very slow. After this the excited atoms rapidly decay to ^3P , which is supposed to be inverted with respect to the ground ^1S state, producing a 6572 \AA laser. See Fig. 10.

A number of other processes may occur, interfering with desired processes. For example



The excited ^1S has 43503 cm^{-1} , which compares to a range due to fine structure of 43701 cm^{-1} to 43822 cm^{-1} on the left hand side. The resonance is close and the reaction is spin-allowed. If this reaction occurs the excitation energy is lost in the rapid allowed radiation of photons at 11832 \AA and 2853 \AA , which should be readily detectable. Similar reactions between two excited Ca atoms should be possible; a number of highly excited Ca states are nearly resonant, and will rapidly decay

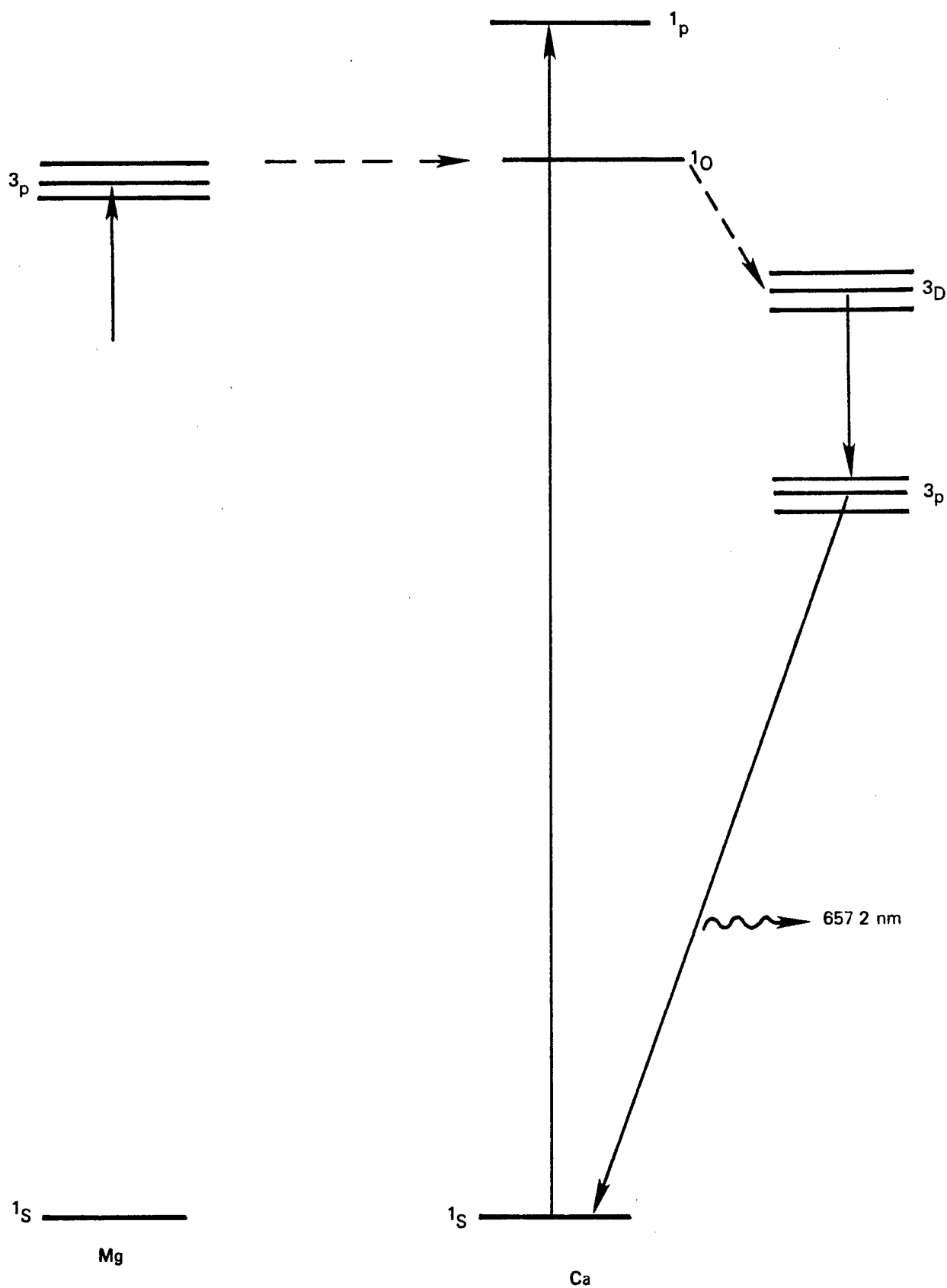


Figure 10 Hypothetical Mg-Ca Energy Flow. (Benard, AFWL)

radiatively. Reactions between excited Ca and excited Mg are also possible. Finally, one must also consider de-excitation of excited Ca and Mg in collisions with other species, such as the noble gases used as buffer gases in these systems. Benard presented a table of Ca de-excitation rate coefficients. He reported that the coefficients for He and Ne were identical to 5%, and only a factor of 3 less than that for Xe. We are skeptical because of the strong variation in polarizability among the noble gases and of a similar variation in the strength of coupling between \vec{L} and \vec{S} .

We found the reported results on Mg-Ca systems quite interesting. There are a number of things we don't understand. That does not prove them wrong, but means that a much greater effort is needed to understand them. Very careful experimental work should be done to be sure that the kinetics are occurring as suggested and not through some very different pathway. Without such an understanding, it is not possible to proceed beyond the stage of basic research.

REFERENCE

1. Eckstrom, D., S. Edelstein and D. Huestis. Stanford Research Institute Memorandum, May 27, 1976.

ACKNOWLEDGEMENTS

The JASON committee gratefully acknowledges briefings from the following experts:

<u>Briefer</u>	<u>Affiliation</u>	<u>Date of Briefing</u>
Dr. R. Taylor	Private Consultant	June 25, 1980
Dr. D. Huestis	SRI International	July 7, 1980
Dr. G. Bosch	KMS	July 7, 1980
Prof. C. Rhodes	University of Illinois in Chicago	July 8, 1980
Dr. Avizonis	Air Force Weapons Laboratory	July 10, 1980
Dr. D. Benard	Air Force Weapons Laboratory	July 10, 1980
Dr. M. Kraus	National Bureau of Standards	July 10, 1980
Dr. W. Rich	Calspan	July 11, 1980
Dr. W. Warren	Aerospace	July 11, 1980

THIS PAGE LEFT BLANK INTENTIONALLY

DISTRIBUTION LIST

ORGANIZATION	NO. OF COPIES	ORGANIZATION	NO. OF COPIES
Dr. Petras Avizonis AWFL/AR Kirtland AFB Albuquerque, NM 87117	1	Dr. Norval Fortson Department of Physics (FM-15) University of Washington Seattle, WA 98195	1
Dr. D. Benard AWFL/AR Kirtland AFB Albuquerque, NM 87117	1	Director National Security Agency Fort Meade, MD 20755 ATTN: Mr. Richard Foss, A42	2
Col. Rhett Benedict DARPA 1400 Wilson Boulevard Arlington, VA 22209	1	Dr. Robert Fossum, Director DARPA 1400 Wilson Boulevard Arlington, VA 22209	2
Dr. G. Busch KMS 3621 S. State Street Ann Arbor, MI 48106	1	Dr. Edward A. Frieman Director, Office of Energy Research, U.S.DOE M.S. 6E084 Washington, D.C. 20585	1
Dr. Gregory Canavan Director, Office of Inertial Fusion, U.S. DOE M.S. C404 Washington, D.C. 20545	1	Dr. George Gamota OUSDRE (R&AT) Room 3D1067, The Pentagon Washington, D.C. 20301	3
Dr. Robert Clark P.O. Box 1925 Washington, D.C. 20013	1	Director National Security Agency Fort Meade, MD 20755 ATTN: Mr. Thomas Handel, A243	1
Cmdr. Robert Cronin NFOIO Detachment, Suitland 4301 Suitland Road Washington, D.C. 20390	1	Dr. William Happer 6 Edgehill Street Princeton, NJ 08540	1
Dr. James Davis Lawrence Livermore Lab Livermore, CA 94550	1	Dr. Benjamin Huberman Associate Director, OSTP Room 476, Old Executive Office Building Washington, D.C. 20506	1
Defense Documentation Center Cameron Station Alexandria, VA 22314	3	Dr. David Huestis SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1
Dr. David D. Elliott SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1		

ORGANIZATION	NO. OF COPIES	ORGANIZATION	NO. OF COPIES
Dr. Jonathan I. Katz Department of Astronomy University of California Los Angeles, CA 90024	1	Dr. Julian Nall P.O. Box 1925 Washington, D.C. 20013	1
Mr. Eugene Kopf Principal Deputy Assistant Secretary of the Air Force (RD&L) Room 4E964, The Pentagon Washington, D.C. 20330	1	Prof. William A. Nierenberg Scripps Inst. of Oceanography University of California La Jolla, CA 92093	1
Dr. Morris Krauss Room B268, Building 221 Division of Molecular Spectroscopy National Bureau of Standards Washington, D.C. 20234	1	Prof. Charles Rhodes Department of Physics University of Illinois P.O. Box 4348 Chicago, Illinois 60680	1
Mr. Ray Leadabrand SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1	Dr. William Rich Calspan Corp. P.O. Box 400 Buffalo, NY 14225	1
Mr. Barry Leven NISC/Code 20 4301 Suitland Road Washington, D.C. 20390	1	Mr. Paul Robinson Los Alamos Scientific Laboratory P.O. Box 1663 Los Alamos, NM 87545	1
Dr. Donald M. LeVine SRI International 1611 N. Kent Street Arlington, VA 22209	3	Mr. Robert Sepucha DARPA 1400 Wilson Boulevard Arlington, VA 22209	1
Director National Security Agency Fort Meade, MD 20755 ATTN: Mr. Robert Madden, R/SA	2	Dr. Ray Taylor Research & Laser Technology 6 Frank Street Rockport, MA 01966	1
Dr. Joseph Mangano DARPA 1400 Wilson Boulevard Arlington, VA 22209	1	SRI/MP Reports Area G037 333 Ravenswood Avenue Menlo Park, CA 94025 ATTN: D. Leitner	2
Mr. John Meson DARPA 1400 Wilson Boulevard Arlington, VA 22209	1	Ms. Alice Wright SRI International 333 Ravenswood Avenue Menlo Park, CA 94025	1